

Isolation of a New Fraction from Wool Wax Acids

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By the saponification of wool wax and the isolation of the acid fraction free of all alkali-insoluble material, it has been possible to separate chromatographically from the "acid" fraction a non-acidic material which appears to be a lactone of molecular formula $C_{20}H_{38}O_2$ representing 12% of the acid fraction. This material gave negative tests for nitrogen by the soda lime test, for unsaturation using bromine in carbon tetrachloride and for aldehyde or ketone using 2,4-dinitrophenylhydrazine reagent. Additional efforts to saponify this material and obtain an unsaponifiable fraction were unsuccessful. Infrared examination of the lactone fraction dissolved in carbon disulfide showed a carbonyl absorption band at 1738 kaysers¹ which agrees closely with a literature value² of 1740 kaysers for a δ -lactone carbonyl. The spectrum of the lactone fraction showed no absorption band near the higher frequency (1770 kaysers) given in the literature² for γ -lactones. On the other hand, authentic samples of γ -stearolactone, γ -valerolactone and γ -butyrolactone showed carbonyl bands at 1784, 1788 and 1786 kaysers, respectively.

Refluxing the lactone with methanol and sulfuric acid as catalyst yielded a derivative, presumably a methyl ester, whose infrared spectrum in carbon disulfide (7.6 g./l.) showed an ester carbonyl absorption band at 1744 kaysers and broad alcoholic hydroxyl absorption bands at 3370 and 3470 kaysers. The total area of these hydroxyl absorptions was appreciably less than that of methyl 12-hydroxystearate, whose major hydroxyl band occurred at 3630 kaysers with minor broad bands at 3370 and 3470 kaysers (8.7 g./l. in CS_2). The original lactone showed no hydroxyl bands.

The ease of δ -lactone formation is well established. From the data obtained it may be inferred

that the lactone fraction is a δ -lactone. Such a compound would explain the difficulty encountered in obtaining wool wax acids free of an appreciable saponification number. Furthermore, the above data would indicate the presence of a δ -hydroxy acid in wool wax acids. Thus far the only hydroxy acids isolated from wool wax were α -hydroxy acids.³⁻⁶

Although the information available indicates the probability that the lactone is a $C_{20}H_{38}O_2$ compound, the data do not eliminate the possibility that we have a difficultly separable mixture of δ -lactones.

Experimental

A 500-g. sample of U.S.P. lanolin was saponified⁷ and the resulting mixture was exhaustively extracted with petroleum naphtha (88-98°). From the extract there was isolated 243 g. of material having an acid number of 2.66 and a saponification number of 11.97. The soaps remaining in the lower layer in the continuous extractor were acidified with a 100% excess of concentrated hydrochloric acid and the acid mixture heated for four hours at 68°. The mixture was allowed to cool to room temperature and then continuously extracted with ether for 24 hours. The ether extract was evaporated leaving 261 g. of material having an acid number of 103.5 and a saponification number of 167.5. A 15-g. sample of this material in 30 ml. of reagent grade chloroform was chromatographed on a 4.5 cm. \times 39 Florisil column.

The column was developed with petroleum ether (35-60°) (8 liters eluted 10% and an additional 12 liters eluted 2% more by wt.). The residue obtained by evaporating 20 liters of petroleum ether weighed 1.8 g. and contained no free acid.

Anal. Calcd. for $C_{20}H_{38}O_2$: sapon. equiv., 310.5; C, 77.36; H, 12.33. Found: sapon. equiv., 311.1; C, 77.7; H, 12.8; $[\alpha]^{25}_D + 13^\circ$ (chloroform, $c = 4$); mol. wt. (cryoscopically in benzene), 316.

Methanolysis.—A 0.68-g. sample of lactone was refluxed for 6 hours with 250 ml. of methanol and 2 drops of concentrated sulfuric acid. The reaction mixture was diluted with 200 ml. of water, concentrated to approximately 200 ml. and ether-extracted. The organic layer was washed free of acid with water and then dried over anhydrous granular sodium sulfate. The dry extract was evaporated leaving a residue of 0.78 g., $[\alpha]^{25}_D + 5.0^\circ$ (chloroform, $c = 1.8$).

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